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(54) Title: CLEANING COMPOSITIONS AND THEIR USE

(57) Abstract: A cleaning composition contains the components for a pH step reaction, held apart or in stasis in needed, until they are delivered to the locus to be cleaned. The composition may include standard cleaning agents such as surfactants. The composition undergoes a change in pH at the locus, promoting effective cleaning.

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CLEANING COMPOSITIONS AND THEIR USE

This invention relates to cleaning compositions and their use.

5

Bathroom cleaners are mainly acidic compositions, intended to combat calcium deposits. On the other hand kitchen cleaners are mainly alkaline compositions, intended to combat grease deposits. However there are 10 situations in which for bathroom cleaning, an alkaline composition is required; and in which for kitchen cleaning, an acidic cleaning composition is required. The customer has to decide whether to purchase a plethora 15 of different products for different cleaning tasks, or whether to compromise. It would be good to have a single composition which was able to combat the deposits attacked by acidic cleaning compositions and the deposits attacked by alkaline cleaning compositions, but the difficulty in achieving this is self-evident.

20

It would also be advantageous to have a cleaning composition which is initially acidic or alkaline, to effect cleaning, but which does not remain so, in order to prevent damage to a substrate and, if wished, to 25 effect a second stage of cleaning.

In accordance with a first aspect of the present invention there is provided a cleaning composition which comprises reactants which undergo a chemical reaction 30 after exposure to a locus to be cleaned, the reaction being such as to produce a delayed change of pH at that locus.

In accordance with a second aspect of the present invention there is provided a cleaning composition having the property that on exposure to a locus to be cleaned the locus renders acidic or alkaline or neutral, and that 5 after an interval it renders the locus alkaline or neutral (if originally acidic) or acidic or neutral (if originally alkaline) or acidic or alkaline (if originally neutral).

10 The composition of any of the aspects may have the property that the locus containing the composition is initially an acidic liquid and after an interval becomes an alkaline liquid.

15 The composition of any of the aspects may have the property that the locus containing the composition is initially an alkaline liquid and after an interval becomes an acidic liquid.

20 Preferably the pH change takes place after an induction period (that is, an interval after exposure of the composition to the locus) of at least 10 seconds, more preferably at least 20 seconds, most preferably at least 60 seconds, and, especially, at least 100 seconds.

25

Suitably the said induction period is not more than 12 hours, preferably not more than 1200 seconds, more preferably not more than 600 seconds, most preferably not more than 400 seconds, and, especially, not more than 300 30 seconds.

A composition of the invention could be a single-pack composition, with the reactants being held in stasis if necessary. In such embodiments the pH change which takes place may be initiated by addition of an agent from which 5 the reactants were previously protected. For example, it could be water, or oxygen, or carbon dioxide, or light.

Alternatively the reactants could be kept physically separated from each other prior to their use, as for 10 example in a tablet or dissolvable sachet having two or more zones, which may be layers, portions or encapsulated sections, depending on the type of tablet or sachet, or in a twin-bottle package or twin-tablet package. In all such embodiments the key measure is that the reactants 15 are combined only at the time of cleaning.

The composition may be provided in a package which emits the composition as a spray, mousse, gel or liquid jet. The package may suitably be a trigger spray or, 20 preferably, an aerosol canister. A spray-emitting package of the composition, especially an aerosol canister, constitutes a further aspect of the invention. In other embodiments a wipable product, for example a sponge or cloth, is impregnated with a composition.

25

The composition may be a product for dilution in order to be used, or a product in ready-to-use form. When a product is for dilution, it may be a solid, for example a powder or tablet, or a liquid, or a gel.

30

The composition may be provided in packaging giving unit-dose supply of the composition.

The composition may be such that the chemical reaction causes a colour change. One or more of the reactants responsible for the change of pH may cause a change of colour, for example on exhaustion, or a 5 separate dye or colorant may be included in the composition, responsive to pH change or to the presence of oxidant species, or reductant species, or temperature change in the case of an exothermic reaction.

10 Other means of indicating chemical change than colour may be employed. For example the system could be arranged to effervesce when the reaction takes place, for example by including a bicarbonate in a system which becomes acidic after the induction period. Another 15 method useful in the case of an exothermic reaction employs a fragrance rendered volatile by a temperature rise.

The term "cleaning" as used herein may include: 20 removal of soil deposits; prevention of soiling; bleaching; combating of allergens; and combating of microbes, including by one or more of antiseptic, disinfectant, bactericidal, sporicidal, fungicidal and viricidal action.

25

Preferably, the composition is antimicrobial. Preferably an antimicrobial effect is generated by the reaction, for example by temperature rise when the 30 reaction is exothermic and/or by the pH change at the locus and/or by production of an antimicrobial chemical, in the reaction. Preferably an antimicrobial chemical is generated in situ by the reaction which changes the pH,

and therefore with the same delay. The antimicrobial chemical may, for example, comprise an iodate, bromate, thiocyanate or chlorate.

5 The composition preferably produces a bleaching effect. Preferably a bleaching effect is generated by the reaction, for example by the temperature when the reaction is exothermic and/or by the pH change at the locus and/or by production of a bleaching chemical, in
10 the reaction. Preferably a bleaching agent is produced in situ by the reaction which changes the pH, and therefore with the same delay. For example, the composition may include sodium chlorite generating, under acid conditions, sodium hydroxide and chlorine dioxide.
15 Thus, both a bleaching agent and an alkaline agent may be generated.

Suitably the composition may contain hydrogen peroxide or a precursor to it as a bleaching agent and/or
20 reactant.

The composition may include one or more surfactants. A surfactant used in the present invention may be selected from one or more surfactants which may be
25 anionic, cationic, nonionic or amphoteric (zwitterionic) surface active agents.

One class of nonionic surfactants which may be used in the present invention are alkoxylated alcohols,
30 particularly alkoxylated fatty alcohols. These include ethoxylated and propoxylated fatty alcohols, as well as ethoxylated and propoxylated alkyl phenols, both having

alkyl groups of from 7 to 16, more preferably 8 to 13 carbon chains in length.

Examples of alkoxylated alcohols include certain 5 ethoxylated alcohol compositions presently commercially available from the Shell Oil Company (Houston, TX) under the general trade name NEODOL (trade mark), which are described to be linear alcohol ethoxylates and certain compositions presently commercially available from the 10 Union Carbide Company, (Danbury, CT) under the general trade name TERGITOL (trade mark) which are described to be secondary alcohol ethoxylates.

Examples of alkoxylated alkyl phenols include 15 certain compositions presently commercially available from the Rhône-Poulenc Company (Cranbury, NJ) under the general trade name IGEPAL (trade mark), which are described as octyl and nonyl phenols.

20 Another class of non-ionic surfactants that may be used are sorbitan esters of fatty acids, typically of fatty acids having from 10 to 24 carbon atoms, for example sorbitan mono oleate.

25 Examples of anionic surface active agents which may be used in the present invention include but are not limited to: alkali metal salts, ammonium salts, amine salts, aminoalcohol salts or the magnesium salts of one or more of the following compounds: alkyl sulphates, 30 alkyl ether sulphates, alkylamidoether sulphates, alkylaryl polyether sulphates, monoglyceride sulphates, alkylsulphonates, alkylamide sulphonates,

alkylarylsulphonates, olefinsulphonates, paraffin sulphonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfosuccinamate, alkyl sulfoacetates, alkyl phosphates, 5 alkyl ether phosphates, acyl saronsinates, acyl isothionates and N-acyl taurates. Generally, the alkyl or acyl group in these various compounds comprises a carbon chain containing 12 to 20 carbon atoms.

10 Other anionic surface active agents which may be used include fatty acid salts, including salts of oleic, ricinoleic, palmitic and stearic acids; copra oils or hydrogenated copra oil acid, and acyl lactylates whose acyl group contains 8 to 20 carbon atoms.

15 Amphoteric surfactants which may be used in the present invention including amphoteric betaine surfactant compounds having the following general formula:

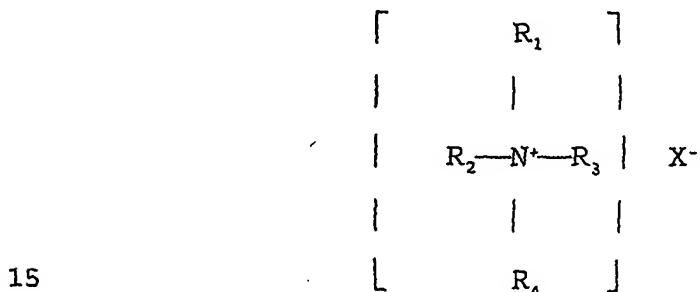
$$20 \quad (+) \quad (-) \\ R-N(R_1)_2-R_2COO$$

wherein R is a hydrophobic group which is an alkyl group containing from 10 to 22 carbon atoms, preferably from 12 to 18 carbon atoms, an alkylaryl or arylalkyl group containing a similar number of carbon atoms with a benzene ring being treated as equivalent to about 2 carbon atoms, and similar structures interrupted by amido or ether linkages; each R₁ is an alkyl group containing from 1 to 3 carbon atoms; and R₂ is an alkylene group containing from 1 to 6 carbon atoms.

One or more such betaine compounds may be included in the compositions of the invention.

Examples of cationic surfactants which may be used 5 in the present invention include quaternary ammonium compounds and salts thereof, including quaternary ammonium compounds which also have germicidal activity and which may be characterized by the general structural formula:

10



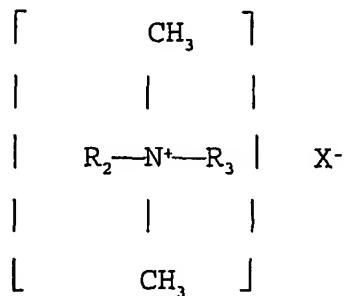
when at least one of R_1 , R_2 , R_3 and R_4 is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl group containing from 6 to 26 carbon atoms, and the entire 20 cationic portion of the molecule has a molecular weight of at least 165. The hydrophobic groups may be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl or aryl alkyl. The remaining 25 groups on the nitrogen atoms, other than the hydrophobic radicals, are generally hydrocarbon groups usually containing a total of no more than 12 carbon atoms. R_1 , R_2 , R_3 and R_4 may be straight chain or may be branched, but are preferably straight chain, and may include one or 30 more amide or ester linkages. X may be any salt-forming anionic moiety.

Examples of quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium 5 bromide, and N-alkyl pyridinium halides such as N-cetyl pyridinium bromide. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide or ester linkages, such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride 10 and N-(laurylcocoaminoformylmethyl)-pyridinium chloride. Other effective types of quaternary ammonium compounds which are useful as germicides includes those in which the hydrophobic moiety is characterized by a substituted 15 aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulphate, dodecylphenyltrimethyl ammonium methosulphate, dodecylphenyltrimethyl ammonium chloride and chlorinated dodecylphenyltrimethyl ammonium chloride.

20

Preferred quaternary ammonium compounds which act as germicides and which are useful in the present invention include those which have the structural formula:

25



30

wherein R₂ and R₃ are the same or different C₈-C₁₂alkyl, or R₂ is C₁₂-C₁₆alkyl, C₈-C₁₈alkylethoxy, C₈-C₁₈alkyl-phenolethoxy and R₃ is benzyl, and X is a halide, for example chloride, bromide or iodide, or methosulphate.

5 Alkyl groups R₂ and R₃ may be straight chain or branched, but are preferably substantially linear.

A mixture of two or more surface active agents may also be used. Other known surface active agents not 10 particularly described above may also be used. Such surface active agents are described in McCutcheon's Detergents and Emulsifiers, North American Edition, 1982; Kirk-Othmer, Encyclopaedia of Chemical Technology, 3rd Ed., Vol. 22, pp 346-387.

15

The compositions of the present invention may include therein one or more organic solvents, such as lower alkyl alcohols, lower alkyl diols or glycol ethers. Such compounds may function as a cleaning agent of the 20 compositions, and may be especially useful in glass cleaners due to their lack of tendency to smear.

Preferably the composition is such that after exposure to an locus to be cleaned its temperature rises, 25 preferably caused by the reaction which changes the pH, and therefore with the same delay. Thus, the reaction responsible for change in pH is preferably exothermic.

The composition may be such that after one pH change 30 the pH may change in the reverse direction. For example a composition may go from acidic to alkaline and back to to acidic, or from alkaline to acidic and back to

alkaline. It is possible that such compositions may undergo further pH changes. Each pH change preferably takes place over an induction period as defined above.

5 Thus, cleaning compositions based on pH-oscillatory systems may be envisaged. Suitable systems may include those described in the following references:

Oscillation, Waves and Chaos in Chemical Kinetics, S.K.
10 Scott, Oxford University Press, 1995.

Design of pH-Regulated Oscillators, G. Rabai et al,
Acc.Chem.Res., 1990, 23, 258-263.

A General Model for pH Oscillators, Y. Luo et al, J. Am.
Chem. Soc., 1991, 113, 1518-1522.

15 Temperature compensation in the oscillatory hydrogen peroxide-thiosulfate-sulphite flow system, G. Rabai et al, Chem. Commun., 1999, 1965-1966.

Kinetic Role of CO₂ in the Oscillatory H₂O₂-HSO₃⁻ - HCO₃⁻
Flow System - G. Rabai et al, J. Phys. Chem. A1999, 103,
20 7224-7229.

Chaotic pH oscillations in hydrogen peroxide-thiosulfate-
sulphite flow system, G. Rabai et al, J. Phys. Chem.
A1999, 103, 7268-7273.

25 Thus, preferably the composition may contain components which provide an abrupt pH step. The autocatalytic species for the reaction is H⁺ (or, more rarely, OH⁻) and pH steps may occur when a solution of a weak acid is oxidised to provide a strong acid, so that
30 H⁺ concentration increases with the extent of reaction.

The chemical composition of a typical pH step system will involve an oxidant and a reductant. Typically, the reductant will be the salt of a weak acid and the corresponding oxidant will be a strong acid. Of course, 5 a reaction may employ a plurality of oxidants and/or a plurality of reductants.

Many different species can be used as partners in these redox systems. In seeking appropriate species, a 10 useful guide for the overall reaction stoichiometry is that the reducing agent should release more protons per electron than the oxidising agent consumes.

Within the existing literature, the following species 15 can be identified and may be of use in cleaning compositions:

Potential oxidant:

20 I peroxyo-compounds (eg BrO_3^- , IO_3^- , ClO_3^- , ClO_2^- , $\text{S}_2\text{O}_8^{2-}$, ClO_2 , H_2O_2 or a precursor thereof)

II oxidising metal compounds stable in alkaline solutions (eg $[\text{Fe}(\text{CN})_6]^{3-}$).

25

Potential reductant:

I all oxyanions of sulphur that contain S-S bonds (eg $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_6^{2-}$).

30

II reducing agents that are significantly more basic than their oxidised counterparts (eg SO_3^{2-} , HSO_3^- , AsO_3^{3-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, N_2H_5^+ , $[\text{Fe}(\text{CN})_6]^{4-}$).

5 Based on reactions described in the published literature, a matrix of combinations from some of these species can be constructed:

Reductant	$\text{S}_2\text{O}_3^{2-}$	$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_4^{2-}$	SO_3^{2-}	$\text{S}_2\text{O}_6^{2-}$	N_2H_5^+
oxidant						
BrO_3^-	Yes	Yes	Yes	Yes	Yes	Yes
IO_3^-	No	No	Yes	Yes	Yes	Yes
ClO_3^-	No	Yes	No	No	Yes	No
ClO_2^-	Yes	Yes	Yes	Yes	Yes	Yes
$\text{S}_2\text{O}_8^{2-}$	Yes	Yes	Yes	Yes	Yes	Yes

10 where "Yes" indicates established evidence for pH step behaviour and "No" indicates no observed reaction under conditions investigated to date.

15 The most widely studied pH step reactions are those typified by the Landolt clock reaction, in which the oxidant is of formula XO_n^- when X is Cl, Br or I and n is 3 when X is Br or I, and 2, 3 or 4 when X is Cl; and the reductant is $\text{SO}_3^{2-}/\text{HSO}_3^-$. The classic Landolt system employs IO_3^- as oxidant and is $\text{SO}_3^{2-}/\text{HSO}_3^-$ as reductant.

20 The reaction is autocatalytic in I^- (depending on the second power of the iodide ion concentration) and is a pH step reaction system even in buffered solution. In unbuffered solution, the reaction is also autocatalytic in H^+ .

Beyond those combinations mentioned above, there are reports of pH step reactions with associated pH changes involving the following reagents:

5 permanganate ion as oxidant with reductant being sulphite, nitrite, selenite, arsenite thiosulfate + iodide + H₂O₂ or a precursor thereof.

Examples of precursors of hydrogen peroxide include urea hydrogen peroxide (UHP) and a cyclodextrin complexed 10 with an organic peroxy acid, for example as described in EP-A-895777. An example is β -cyclodextrin complexed with an organic peroxy acid, ϵ -phthalimido peroxyhexanoic acid (PAP). This product is available under the trade mark EURECO HC from Wacker Chemie GmbH.

15

The addition of a second reductant to a Landolt system ("mixed-Landolt system") may produce a pH step reaction in which the pH swings from high to low at the 20 end of an induction period, and then back to high pH on a longer timescale.

An example of a pH step reaction system starting at low pH and changing to high pH at the end of an induction period involves the reduction of H₂O₂ (which may be 25 delivered by means of a precursor, as described above) by various multidentate complexes of Fe(II) or Co(II) ions, notably using Fe(CN)₆⁴⁻ as the anion species, as described in G. Rabai et al, J.Am.Chem.Soc., 1989, III, p. 3870.

30 Cleaning compositions of the invention may be used, for example, for textile materials, including carpets and clothes. They may be used in dishwasher cleaning

compositions and clothes washing compositions. The change of pH may, for example, initiate the dissolution of the coating of a washing tablet or of an insert product contained within a washing tablet, providing in
5 each case delayed release of the contents.

A preferred cleaning composition of the present invention is a hard surface cleaner, for cleaning ceramics, glass, stone, plastics and wood; and 10 particularly for cleaning bathroom and kitchen hard surfaces, for example sinks, bowls, toilets, panels, tiles and worktops. When acidic it is particularly effective in combating limescale. When alkaline it is particularly effective in combating grease and 15 proteinaceous deposits.

Another preferred cleaning composition is adapted for cleaning dentures (normally of polyacrylic material) and is therefore effective in removing staining and/or 20 plaque.

Another preferred cleaning composition is adapted for cleaning lavatory bowls and for this purpose the composition may be packaged in an ITB (In the Bowl) or 25 ITC (In the Cistern) device, preferably in a holder which hangs from the rim of the bowl or cistern. In the case of chemical reactants which are desirably kept apart until cleaning takes place the reactants are preferably liquids kept in separate vessels, or solids formulated in 30 separate tablets (for example compressed powders or granules, or gel blocks) or in one tablet with distinct zones for the different reactants. Of course, in some

systems the reactants may be mixed and only react in use, in which case a single vessel or simple tablet may be used.

5 Another useful cleaning composition is adapted to clean marble surfaces effectively. Such a composition is acidic when applied in order to attack certain stains and soils, but becomes alkaline before any dissolution of the marble can occur. When alkaline it attacks other stains
10 and soils, notably greases.

The invention will now be further described, by way of example, with reference to the following examples. Unless otherwise stated solutions of the reactants in
15 distilled water were mixed at ambient temperature and stirred with a magnetic stirrer, whilst pH and temperature were monitored. Cationic species were sodium ions.

20 Example 1

The variations of the induction period (the period between mixing of reactants and commencement of pH swing) and of pH swing with initial reactant concentrations for
25 a dilute solution of bromate and sulphite ions, mixed as solutions at ambient temperature, and using concentrated sulphuric acid to adjust the pH, were determined in a series of experiments. As can be seen from Table 1 below, the induction period t_{ind} can be varied between 4
30 hours and 2 minutes, with t_{ind} being approximately inversely proportional to the initial concentrations of both BrO_3^- and H^+ and independent of the initial

concentration of SO_3^{2-} . The initial sulphite concentration appears to determine the pH swing, which is typically of the order of 4 to 5 pH units. The reaction occurs for compositions with initial pH values in the 5 range 6.6 to 8.9.

Table 1

$$[\text{BrO}_3^-]_0 = 0.06 \text{ M}, [\text{SO}_3^{2-}]_0 = 0.054 \text{ M}$$

10

Initial pH	Final pH	pH change	t_{ind}
8.85	3.65	5.2	14400
8.5	3.4	5.1	9000
8.2	2.9	5.3	5580
8.0	2.7	5.3	4080
7.48	2.4	5.08	1320
7.18	2.25	4.93	695
6.9	2.15	4.75	390
6.57	2.04	4.53	140

The initial experiments were repeated varying the initial concentration of bromate ions in a sequence, with 15 constant initial pH and sulphite concentration. This yielded the variations in induction period shown in Table 2 below.

Table 2

$[\text{BrO}_3^-]_0/\text{M}$	0.06	0.054	0.048	0.042	0.036	0.030	0.024
t_{ind}/s	285	350	390	465	470	660	810

20

The initial experiments were then repeated with variations in the concentration of the reductant species sulphite, at constant bromate and initial pH. The effect of this on the induction period and pH swing is set out 5 in Table 3 below.

Table 3

$[SO_3^{2-}]_0$	t_{ind}/s	Final pH
0.054	300	1.95
0.0486	325	1.95
0.0432	310	2.0
0.0324	290	2.0
0.027	305	2.05
0.0216	305	2.1

10 with $[BrO_3^-]_0 = 0.06$ M and an initial pH = 7.0.

Thus in these experiments induction period and pH swing were relatively insensitive to $[SO_3^{2-}]_0$.

15 Overall, the results showed that the system is of value as the basis for a new cleaning composition.

Example 2

20 A series of experiments were run with substantially higher concentrations of the reactants than used in Example 1, with the aim of using the concentration dependence to reduce the induction period whilst maintaining a large pH swing. Also, rather than 25 adjusting the initial pH with concentrated sulphuric acid

after dissolution of the reactants, the required initial pH was attained by using an appropriate mixture of sulphite and bisulphite salts. The variations with initial reductant concentrations of the induction period, 5 final pH and the peak temperature observed during the reaction are given in Table 4 below. The results showed that the system could provide the basis of a promising new cleaning composition.

10

Table 4

$[\text{BrO}_3^-]_0$ /M	$[\text{SO}_3^{2-}]_0$ /M	$[\text{S}_2\text{O}_5^{2-}]_0$ /M	Initial pH	t_{ind}/s	Final pH	Peak temp/°C
0.27	0.516	0.018	7.9	438	2.1	48
0.27	0.555	0.018	7.95	432	2.1	49
0.27	0.62	0.018	7.95	438	2.1	56
0.27	0.674	0.018	7.95	580	2.1	54
0.27	0.754	0.018	8.0	77	2.4	54
0.3	0.516	0.018	7.85	374	2.1	46
0.3	0.555	0.018	7.95	418	2.1	50
0.3	0.62	0.018	7.95	358	2.2	57
0.3	0.67	0.018	8.0	395	2.2	58.5
0.3	0.674	0.018	8.0	395	2.2	58.5
0.3	0.754	0.018	8.05	608	2.3	57
0.35	0.56	0.021	7.85	238	2.05	53
0.35	0.6	0.021	7.95	262	2.1	54
0.35	0.63	0.021	7.9	284	2.1	56
0.35	0.71	0.021	8.05	314	2.2	59
0.35	0.79	0.021	8.05	347	2.35	61
0.35	0.875	0.021	8.05	423	2.5	60
0.4	1.0	0.026	8.0	227	2.5	77

0.539	1.24	0.042	8.0	97	2.4	93
0.539	1.24	0.036	8.2	142	2.7	92
0.539	1.24	0.03	8.4	178	3.0	
0.539	1.24	0.024	8.8	532	4.0	70
0.6	1.24	0.024	8.7	325	3.8	78

Example 3

In this example the classic iodate-sulphite/bisulphite Landolt reaction was examined. The induction period is well known to be inversely proportional to the initial iodate ion concentration and to be independent of the initial sulphite ion concentration (provided the initial pH is maintained constant). The dependence of t_{ind} on the initial pH is less well understood, so these data were determined in the present programme. The solutions were of concentration 0.01M iodate (fixed) and 0.02-0.002M bisulphite. The results are set out in Table 5 below.

In all cases the final pH was 2.2-2.3.

Table 5

pH ₀	6.8	7.0	7.2	7.3	7.4	7.5	7.6	7.7	7.8	7.8
t_{ind}/s	27	62	48	78	90	198	220	480	450	600

Example 4

The chlorate ion ClO_3^- can also be used as the oxidant in Landolt-type systems. A series of experiments were performed on this system. The reaction does not

appear to occur starting from pH values higher than ca. 5.0, so the initial pH was adjusted using concentrated H_2SO_4 to the range 4.5-5.0 for the experiments reported below. The reaction is strongly exothermic and even for 5 relatively dilute solutions, significant temperature rises (self-heating) occur. The results are set out in Table 6 and 7 below.

10 Table 6 - variation of induction period with initial chlorate concentration

$[SO_3^{2-}]_0 = 0.44 \text{ M}$, initial pH = 4.5

$[ClO_3^-]_0/\text{M}$	t_{ind}/s	Final pH	Peak temperature/°C
0.29	128	0.4	45.0
0.264	155	0.5	43.0
0.235	177	0.7	40.5
0.206	220	0.8	38.0
0.177	240	1.0	35.3
0.147	260	1.1	33.0
0.118	337	1.3	31.0

Table 7 - dependence on initial sulphite concentration

$[ClO_3^-]_0 = 0.290 \text{ M}$, initial pH = 4.5

$[SO_3^{2-}]_0/\text{M}$	t_{ind}/s	Final pH	Peak temperature/°C
0.44	128	0.4	45.0

0.409	162	0.4	43.0
0.364	120	0.5	41.0
0.321	110	0.5	39.5

These data indicate that the induction period is inversely proportional to the initial chlorate ion concentration and effectively independent of the sulphite 5 concentration. The peak temperature rise decreases as the system is diluted. The system is of potential value as a cleaning composition.

Example 5

10

A series of experiments were performed in which chlorite ion was added to the bromate-sulphite reaction system to see if the latter could drive the production of ClO₂ after a suitable induction period. The experimental 15 data set out in Table 8 below was collected.

Table 8

$[\text{BrO}_3^-]_0$ /M	$[\text{SO}_3^{2-}]_0$ /M	$[\text{S}_2\text{O}_5^{2-}]_0$ /M	$[\text{ClO}_2^-]_0$ /M	pH_0	$t_{ind}/$ s	Final pH	Peak temp/ °C
0.35	0.56	0.021	0.022	8.05	245	2.15	51
0.35	0.56	0.021	0.055	8.05	221	2.2	51
0.35	0.56	0.021	0.112	8.15	260	2.7	52
0.175	0.28	0.0105	0.0275	7.95	840	2.35	31
0.175	0.28	0.0105	0.0385	8.15	853	2.5	34
0.175	0.28	0.0105	0.055	8.15	690	2.55	33
0.175	0.28	0.0105	0.0825	8.3	865	3.05	35
0.175	0.28	0.0105	0.11	8.45	1005	3.65	
0.175	0.28	0.0132	0.11	8.15	630	2.65	38
0.175	0.28	0.0158	0.165	8.1	289	3.2	
0.175	0.28	0.0184	0.165	7.6	50	2.7	38
0.156	0.28	0.0132	0.111	7.9	475	2.6	35
0.168	0.28	0.0132	0.111	8.0	348	2.5	35
0.175	0.28	0.0132	0.111	8.15	330	2.65	38
0.186	0.28	0.0132	0.111	8.0	333	2.6	36
0.21	0.28	0.0132	0.111	8.0	300	2.6	36
0.175	0.238	0.0132	0.111	7.9	225	2.6	34
0.175	0.258	0.0132	0.111	7.9	278	2.5	35
0.175	0.278	0.0132	0.111	8.15	330	2.65	35
0.175	0.298	0.0132	0.111	8.0	405	2.6	36
0.175	0.317	0.0132	0.111	8.0	557	2.7	36

These results indicate that the system is reasonably robust to the addition of chlorite ion. The induction period and pH change is relatively insensitive to the

chlorite ion concentration, although very high concentrations can inhibit the reaction.

From the drop in pH, it can be expected that the 5 ClO_2^- will decompose to ClO_2 . This has not been confirmed quantitatively, but the presence of ClO_2 was clearly detectable from its smell after the pH change occurred. Thus the system is of potential value for a cleaning agent having sterilizing properties.

10

Example 6

An experiment was carried out to investigate how mixing bromate and sulphite reactants in dry powder form 15 affects induction time, temperature rise and pH. The experiment was carried out for varying sulphite concentration at two initial bromate concentrations (0.4 and 0.6M).

20 The reactants were weighed out in dry powder form so that when mixed with 50ml of water they would give the desired concentrations. Effervescence was seen when the water was added. A comparison was made with reactions using liquid reactants. The results are shown in Table 9 25 below.

Table 9

		[BrO ₃ ⁻]			
		0.4M		0.6M	
		<i>t_{ind}</i>			
[SO ₃ ²⁻]		liquid	dry powder stirred	liquid	dry powder stirred
0.45		177	189	108	116
0.55		189	213	115	130
0.65		207	239	123	150
0.75		229	252	130	160
0.85		268	295	145	172

5 Table 9 above shows how the induction period changes depending on whether the reactants are used in solution or dry powder form. The induction period was increased for the dry powder experiments, but this increase was very small and in most cases only increases the induction
10 time by a few seconds. There was no noticeable difference in the temperature rise and initial and final pH between the dry powder and solution experiments. A powder system was accordingly shown to be of possible value in the present invention.

15

Example 7

20 An experiment was carried out to investigate how using tap water (in the School of Chemistry, University of Leeds, UK) instead of distilled water affects induction period, temperature rise and pH, in a sulphite-bromate system. The experiment was carried out for varying sulphite concentration at two initial bromate

concentrations (0.4 and 0.6M) and a constant bisulphite concentration (0.018M). The results are shown in Table 10 below.

5

Table 10

[SO ₃ ²⁻]	[BrO ₃ ⁻]			
	0.4M		0.6M	
	<i>t_{ind}</i>			
[SO ₃ ²⁻]	distilled water	tap water	Distilled water	tap water
0.45	189	205	116	103
0.55	213	210	130	134
0.65	239	250	150	158
0.75	252	266	160	160
0.85	295	289	172	175

It can be seen from the above results that using tap water instead of distilled water had no significant effect on the induction time with the values staying substantially constant throughout all the experiments. The temperature rise and initial and final pH were also seen to remain substantially constant.

15

Example 8

In a bromate-sulphite system the co-addition of surfactants typically used in household cleaning compositions was studied. A set of initial concentrations were chosen (bromate 0.5M, sulphite 0.65M and bisulphite 0.018M) and a selection of surfactants were added, as identified in Table 11 below.

Table 11

Surfactants	t_{ind}	Max temp (°C)	Initial pH	Final pH	pH swing
None	190	59.5	8.1	2.9	5.2
sodium lauryl sulphate (0.5g)	252	58.5	8.1	2.9	5.2
sodium lauryl sulphate (0.2g)	211	58.0	8.0	2.9	5.1
Empigen BAC 50 (1g)	178	59.5	8.4	3.2	5.2
Polytergent SL-62 (1g)	172	59.5	8.3	3.0	5.3
Dipropylene glycol ether (1g)	182	59.5	8.2	3.0	5.2

5 Sodium lauryl sulphate is a well-known anionic surfactant. Polytergent SL-62 is a non-ionic surfactant, a mixture of ethoxylated and propoxylated fatty alcohols, from BASF. The glycol ether was DOWANOL DPnB glycol ether. Empigen BAC 50 is a cationic surfactant, a benzalkonium chloride, more specifically C_{10-16}

10 (predominantly C_{12-14}) alkyl dimethyl benzylammonium chloride.

15 It can be seen that with the amounts added none of the surfactants has a large effect on the induction time. It can be seen that sodium lauryl sulphate does increase the induction time slightly whereas the Empigen BAC 50, Polytergent SL62 and glycol n-butyl ether all slightly decrease the induction time. The temperature rise in all cases stays constant. The initial pH is slightly raised

20 when Empigen BAC 50, Polytergent SL-62 and glycol n-butyl ether are added but the pH swing stays almost constant.

Example 9

5 A further experiment was carried out to determine in greater detail the effects of adding various surfactants to the bisulphite/sulphite-bromate reaction mixture.

Two different sets of initial concentrations were used:

10 i) bromate 0.5M, sulphite 0.65M and bisulphite 0.018M
ii) bromate 0.7M, sulphite 0.5M and bisulphite 0.018M

A small amount of a common surfactant was added to each experiment in the concentration ranges shown below:

15 Empigen BAC 50: 1% w/w - 5%w/w
Sodium lauryl sulfate: 1% w/w - 5%w/w
Polytergent SL-62: 1% w/w - 10%w/w
Dipropylene glycol n-butyl ether: 1% w/w - 10%w/w

20 Tables 12 and 13 show the results from the experiments. In each case the results are the mean results of three replicates. Table 12 shows the results for the initial concentrations bromate 0.5M, sulphite 0.65M and bisulphite 0.018M and Table 13 shows the results for the initial concentrations bromate 0.7M, sulphite 0.5M and bisulphite 0.018M.

Table 12

Compatibility Tests

Compatibility Tests																							
Empigen BAC 50				Sodium lauryl sulphate				Polytergent SL62				Dipropylene glycol n-butyl ether											
η_{sp}/w	pH_{max}	pH_{min}	ΔpH	η_{sp}/w	pH_{max}	pH_{min}	ΔpH	η_{sp}/w	pH_{max}	pH_{min}	ΔpH	η_{sp}/w	pH_{max}	pH_{min}	ΔpH								
1	8.33	3.00	5.33	192.33	59.33	1	8.08	2.93	5.1	189.00	55.00	2	8.18	2.98	5.20	205.00	57.33	2	8.22	3.00	5.22	197.67	56.17
2	8.60	3.07	5.53	188.33	59.67	2	8.00	2.90	5.1	182.33	55.83	4	8.18	3.00	5.18	209.33	57.17	4	8.20	3.00	5.20	200.33	56.17
3	8.60	3.15	5.45	185.00	59.50	3	8.00	2.90	5.1	180.67	55.83	6	8.22	3.00	5.22	216.00	56.83	6	8.20	3.00	5.20	224.33	55.17
4	8.63	3.25	5.38	161.67	59.83	4	8.00	2.93	5.0	188.67	55.33	8	8.23	3.00	5.23	218.67	57.00	8	8.15	3.00	5.15	234.33	55.17
5	8.62	3.27	5.35	160.00	59.50	5	8.00	2.92	5.0	200.33	55.50	10	8.27	3.07	5.20	219.33	56.33	10	8.18	3.00	5.18	232.67	55.00

Table 13

Compatibility Tests

Compatibility Tests																							
Empigen BAC 50				Sodium lauryl sulphate				Polytergent SL62				Dipropylene glycol n-butyl ether											
%w/w	pH _{max}	pH _{min}	ΔpH	Max T °C	%w/w	pH _{max}	pH _{min}	ΔpH	max T °C	%w/w	pH _{max}	pH _{min}	ΔpH	max T °C									
1	8.20	2.73	5.47	126.00	50.00	1	8.05	2.70	5.35	138.3	50.50	2	8.03	2.73	5.30	129.67	50.00	2	8.10	2.72	5.38	130.33	50.50
2	8.20	2.88	5.32	123.33	50.00	2	8.00	2.70	5.30	138.6	50.00	4	8.03	2.75	5.28	143.67	50.00	4	8.15	2.80	5.35	129.67	50.50
3	8.37	3.00	5.37	127.33	50.00	3	8.00	2.70	5.30	161.3	50.00	6	8.12	2.80	5.32	134.33	50.00	6	8.20	2.80	5.40	135.33	50.00
4	8.48	3.07	5.42	119.00	50.00	4	8.00	2.70	5.30	162.6	49.67	8	8.15	2.88	5.27	136.67	50.00	8	8.17	2.82	5.35	132.33	49.83
5	8.58	3.18	5.40	112.00	49.50	5	8.00	2.70	5.30	174.0	49.33	10	8.15	2.87	5.28	136.67	50.00	10	8.13	2.80	5.33	137.67	49.50

The general conclusion that can be drawn from these more detailed experiments is that none of the surfactants affect the reaction very much. The most 5 important observations are that Empigen BAC 50 seems to decrease the induction time slightly but raises the initial pH by approximately 0.5 units. The initial pH increases with increasing Empigen BAC 50 concentration up to 8.6 (the pH of Empigen BAC 50). Sodium lauryl 10 sulphate slightly increases the induction time.

Example 10

An experiment was conducted to determine whether the 15 dry powder chemicals for the sulphite-bromate system can be stored together and still react when mixed with water

The experiments were conducted as outlined previously, but over a period of 30 days. "Stirred" and 20 "unstirred" variants were carried out. In the "stirred" variants the reaction mixtures were stirred constantly throughout the reactions. In the "unstirred" variants the reaction mixtures were stirred vigorously for 15 seconds, then left unstirred for the rest of the 25 experiments.

It was noted that towards the latter stages of the experiments, orange specks were seen in the powder. Also throughout the experiments it was found that the 30 powder set into a solid lump, which needed to be broken up prior to carrying out the experiments.

The results are shown in Table 14 below.

Table 14

5

Day	Stirred					Unstirred				
	pH _{max}	pH _{min}	ΔpH	t _{ind} /10 s	max T/°C	pH _{max}	pH _{min}	ΔpH	t _{ind} /10 s	max T/°C
1	8.05	2.9	5.15	19.4	59	8.1	2.9	5.2	24	61.5
2	8.05	2.85	5.2	26.1	55	8	2.85	5.15	28.8	58
3	8	2.85	5.15	17.9	59	8.05	2.9	5.15	20.2	61.5
4	8.1	2.9	5.2	19.2	59	8.1	2.9	5.2	19.6	62.5
5	8.1	2.9	5.2	18.6	60.5	8.1	2.9	5.2	28.6	61.5
6	8.05	2.9	5.15	19.3	59	8.1	2.9	5.2	20	60.5
7	8.15	2.95	5.2	21.8	56	8.15	2.95	5.2	35.2	58
8	8.1	2.9	5.2	20.3	56	8.1	2.95	5.15	22.3	58.5
10	8.15	2.95	5.2	23.2	53.5	8.05	2.9	5.15	28.4	56
12	8.15	2.95	5.2	24.7	52	8.1	2.95	5.15	28.7	54.5
14	8.15	2.95	5.2	23	53	8.1	2.95	5.15	26.2	55
16	8.1	2.9	5.2	23.5	52.5	8.05	2.9	5.15	24.3	57
19	8.05	2.9	5.15	24	51	8.1	2.9	5.2	38.6	54
22	8.15	2.95	5.2	22.5	52	8.1	2.9	5.2	35	52
26	8.1	2.9	5.2	21.3	52	8.1	2.95	5.15	33.9	52
30	8.15	2.9	5.25	21.4	55					

It can be seen from Table 14 that in both the stirred and unstirred experiments the initial and final pH stayed almost constant with an initial pH of approximately 8.1 and a final pH of approximately 2.9. The maximum temperature rise also stayed approximately constant at 55°C. The average induction time of the stirred experiments was 216 ± 23.8 s but can be seen to vary in the range of 179 - 261s. The induction time in the unstirred case had an average time of 276 ± 60 s but with times varying from 196 - 386s.

Example 11

Experiments were carried out to investigate a hydrogen peroxide-sulphite/bisulphite system for 5 suitability for use in the present invention. To deliver hydrogen peroxide in a stable manner urea hydrogen peroxide (UHP) $\text{CO}(\text{NH}_2)_2\text{H}_2\text{O}_2$ was used. Sodium sulphite was used in the concentration range $1 \times 10^{-3}\text{M}$ to $5 \times 10^{-3}\text{M}$. UHP was used in the concentration range $1 \times 10^{-2}\text{M}$ to $5 \times 10^{-2}\text{M}$. The experiments showed that induction period for 10 a pH change event could be 80-2000 seconds, with the lower induction periods being promoted by the more concentrated UHP solutions. pH typically swung from an initial pH of 7.5-8.4 (higher with increasing sulphite 15 concentration) to a final pH of 5.1, with UHP concentration having no effect on initial or final pH, and sulphite concentration having no effect on final pH. It was concluded that the system had promise as the basis for a cleaning composition.

20

Example 12

The compatibility of the UHP-sulphite system described in Example 11 with a number of surfactants was 25 also investigated. The following surfactants were tested.

Empigen BAC 50: 1% w/w - 5%w/w

Sodium lauryl sulfate: 1% w/w - 5%w/w

30 Polytergent SL-62: 1% w/w - 10%w/w

Dipropylene glycol n-butyl ether: 1% w/w - 10%w/w

The reactants and their initial concentrations were as follows.

UHP : 0.3M
5 Sulphite : 0.01887M
Bisulphite : 0.00113M

The results are set out in Figures 1 to 4. In these figures the leftmost bar of each block of results was a control (0% w/w surfactant) and the rightmost bar of each block of results denotes the highest concentration of surfactant employed.

The main conclusions are:

- 15 • All the surfactants reduced the initial pH by 0.1 - 0.2 units
- Dipropylene glycol n-butyl ether reduced the final pH. All the other surfactants increased the final pH.
- 20 • All surfactants decreased the induction period. In the case of Empigen BAC 50, the decrease was significant, lowering the induction time by up to a minute at its lowest concentration. Dipropylene glycol n-butyl ether decreased the induction period the least, but still managed to decrease it by 30 seconds at its lowest concentration.
- 25

Example 13

The following samples were tested for antimicrobial properties.

5

Sample 1: Sodium bromate (NaBrO₃) - [0.7M]
Sodium sulphite (NaSO₃) - [0.5M]
Sodium bisulphite (NaS₂O₅) - [0.025M]

10 Sample 2: As Sample 1, but sodium bisulphite concentration 0.018M

In the first tests against *S.aureus* and *E.coli*, testing was undertaken (with Sample 1) using sterile purified water and in the absence of any organic soil. The second tests (with Sample 2) included two additional test organisms (*P.aeruginosa* and *E.hirae*), and were undertaken in hard water (300 ppm CaCO₃) and with the addition of organic soil, bovine serum albumin - BSA.

20

The test method for Sample 2 was as follows: 1ml bacterial suspension (10⁷ cfu/ml) of the selected bacterium was transferred to a flask containing 1ml of a 3% BSA suspension. The culture/ soil mix was vortex mixed and then shaken on an orbital shaker for 2 minutes. To the culture/ soil mix was added 8ml sterile hard water. Mixing was continued for another minute. Without interruption of the shaking, the chemical compounds of the appropriate samples were added to the flask in powder form, in amounts calculated to give the molarities mentioned above. 5 minutes after addition of the sample, shaking was stopped and a 1ml aliquot of the test mixture

was transferred to 9.0ml neutralising medium. After a neutralisation period of 5 minutes, the sample was serially diluted and used to prepare pour plates which were subsequently incubated at 36°C for 48 hours before 5 enumerating surviving bacteria. As an inactive control, testing was repeated without the addition of the test sample. The test method for Sample 1 was similar but as noted above did not employ hard water or BSA.

10 Microbiocidal Effect (ME) values were calculated as follows:

log (cfu/ml in test at t=0) - log (cfu/ml recoverable from test after 5 minute contact time). The results are shown in Tables 15 and 16 below.

15 Table 15. Median ME values (n=3), for *S.aureus* and *E.coli* in preliminary tests

Test organism	Median ME values	
	(Sample 1)	Water (control)
<i>S.aureus</i>	>5.7	0.1
<i>E.coli</i>	>5.4	0.1

Table 16. Median ME values (n=3) from further testing

20

Test organism	Median ME values
<i>S.aureus</i>	5.3
<i>E.coli</i>	5.4
<i>P.aeruginosa</i>	>5.2

On the basis of these preliminary results, it appears that exposure of bacteria to the reactants in a standard suspension test produces considerable reductions in bacterial viability. Reductions in excess of log 5.0 were 5 achieved for all four test organisms in the presence of the organic soil bovine serum albumin and hard water, and with a 5-minute contact time.

Accordingly, it was concluded that the system showed 10 good activity as an antimicrobial cleaning composition.

Example 14

Experiments were carried out on a system postulated 15 to cause an increase in pH, employing urea hydrogen peroxide and $\text{Fe}(\text{CN})_6^{4-}$.

The experiments assessed the effect of concentration of the species above and of hydrogen ion 20 concentration.

Tables 17-19 summarise the results of the experiments. In each case two species were kept at constant concentrations whilst the third was varied.

25

When not being varied, the initial species concentrations were:

- UHP = 2×10^{-3} M
- Ferrocyanide = 2×10^{-3} M
- 30 • $\text{H}^+ = 5 \times 10^{-4}$ M

Table 17

		pH _o	pH _f	ΔpH	t _{ind}
Hydrogen ion concentration/M	1.00E-04	5.7	9.2	3.5	209.2
	2.50E-04	5.1	9.2	4.1	421.0
	5.00E-04	4.8	9.2	4.4	593.3
	7.50E-04	4.5	9.2	4.7	977.0
	1.00E-04	4.3	9.2	4.9	1114.0

(Average of 3 replicates)

5

Table 18

		pH _o	pH _f	ΔpH	t _{ind}
UHP concentration/M	1.25E-03	4.8	9.2	4.4	821.0
	2.00E-03	4.8	9.2	4.4	609.5
	2.50E-03	4.8	9.2	4.4	550.0
	3.75E-03	4.8	9.2	4.4	505.0
	5.00E-03	4.8	9.2	4.4	367.0

(Average of 2 replicates)

Table 19

		pH _o	pH _f	ΔpH	t _{ind}
Ferrocyanide concentration /M	1.25E-03	4.6	8.9	4.4	728.5
	2.00E-03	4.8	9.2	4.5	608.0
	2.50E-03	4.8	9.2	4.4	437.0
	3.75E-03	5.0	9.4	4.4	379.0
	5.00E-03	5.1	9.5	4.4	319.0

5

(Average of 2 replicates)

No temperature rise was observed during any of the experiments. A colour change of colourless to pale yellow was observed. The mean pH increase varied between 10 3.5 and 4.9 and was often 4.4.

Example 15

15 A hard surface cleaning composition has the following composition.

TERGITOL secondary alcohol	0.6% w/w
ethoxylate	
Ethylene glycol-n-butyl ether	
20 (non-ionic surfactant)	
Fragrance	0.2% w/w
Colour	trace

	H ₂ O ₂	0.1% w/w
	Na ₂ S ₂ O ₃	0.16% w/w
	Na ₂ SO ₃	0.05% w/w
	H ₂ SO ₄	0.005% w/w
5	Liquified petroleum gas (propellant)	20% w/w
	Deionised water	to 100% w/w

During preparation the hydrogen peroxide was kept
 10 separate from a solution of the three sulfur-containing
 compounds. These input solutions were kept free of air
 before mixing and were mixed in the absence of air, and
 bottled in aerosol cans, free of air. Only on spraying a
 surface with this composition, for cleaning, does the pH
 15 step reaction start.

Example 16

	A hard surface cleaner has the following composition:	
20	Ethoxylated fatty alcohol (C ₁₂₋₁₄ ; 3EO)	1% w/w
	(non-ionic surfactant)	
	Ethylene glycol	5% w/w
	Fragrance	0.1% w/w
25	Colour	trace
	NaIO ₄	0.43% w/w
	Na ₂ S ₂ O ₃	0.16% w/w
	Na ₂ SO ₃	0.06% w/w
	H ₂ SO ₄	0.01% w/w
30	Butane (propellant)	18% w/w
	Deionised water	to 100% w/w

The components were mixed and loaded into spray canisters with exclusion of air. Only on spraying a surface with this composition, for cleaning, does the pH step reaction start.

CLAIMS

1. A cleaning composition which comprises reactants which undergo a chemical reaction after exposure to a locus to be cleaned, the reaction being such as to produce a delayed change of pH at that locus.
5
2. A composition as claimed in claim 1, having the property that after exposure to the locus the composition produces a delayed change of pH at that locus of at least 10 2 pH units.
3. A composition as claimed in claim 1 or 2, having the property that after exposure to the locus the composition produces a delayed increase in pH at that locus.
15
4. A composition as claimed in claim 3, having the property that on exposure of the composition to the locus the locus is initially acidic and that after an interval 20 the locus is alkaline.
5. A composition as claimed in claims 3 or 4, wherein the composition comprises hydrogen peroxide or a precursor of hydrogen peroxide and a multidentate complex 25 of Fe (II) or Co (II) ions.
6. A composition as claimed in claim 1 or 2, having the property that after exposure to the locus it produces a delayed decrease in pH at that locus.
30
7. A composition as claimed in claim 6, wherein the composition comprises an oxidant selected from a peroxy

compound and an oxidising metal compound stable in alkaline solutions; and a reductant selected from an oxyanion of sulfur that contains S-S bonds, and a compound substantially more basic than its oxidised 5 counterpart.

8. A composition as claimed in claim 7, wherein the oxidant is selected from the species BrO_3^- , IO_3^- , ClO_3^- , ClO_2^- , $\text{S}_2\text{O}_8^{2-}$, ClO_2 , $[\text{Fe}(\text{CN})_6]^{3-}$ and H_2O_2 or a precursor 10 thereto, and the reductant is selected from the species $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_6^{2-}$, SO_3^{2-} and N_2H_5^+ , the oxidant and the reductant together participating in reactions producing pH oscillations.

15 9. A composition as claimed in any preceding claim, wherein the composition produces an antimicrobial effect at the locus.

10. A composition as claimed in any preceding claim, 20 wherein the composition produces a bleaching effect at the locus.

11. A composition as claimed in any preceding claim, 25 wherein a temperature rise is generated by the reactants at the locus.

12. A composition as claimed in any preceding claim, the composition being such that the pH change is evidenced by a change in colour or fragrance, or by effervescence.

30 13. A composition as claimed in any preceding claim, comprising a surfactant.

14. A composition as claimed in any preceding claim, wherein the composition is packaged with exclusion of oxygen and/or water and/or carbon dioxide and/or light, 5 as required to prevent a pH change prior to exposure to the locus.

15. A tablet or sachet, comprising a cleaning composition as claimed in any preceding claim, in liquid, powder or 10 gel form.

16. A cleaning cloth or sponge, impregnated with a cleaning composition as claimed in any of claims 1 to 14.

15 17. A lavatory cleaning product to be hung or otherwise located in a cistern or beneath the rim of a lavatory bowl and comprising a composition as claimed in any of claims 1 to 14, the product being such that the composition is released progressively with flush water.

20 18. A dispensing package containing a cleaning composition as claimed in any preceding claim, wherein the package emits the cleaning composition progressively, as a spray, gel or mousse.

25 19. A method of cleaning comprising the application of a cleaning composition as claimed in any of claims 1 to 14, to a locus requiring cleaning.

30 20. A cleaning composition or product or package, or a cleaning method, in each case substantially as

hereinbefore described with particular reference to the accompanying examples.

Figure 1

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**Compatibility of the hydrogen peroxide-sulfite-bisulfite reaction with
Empigen BAC 50**

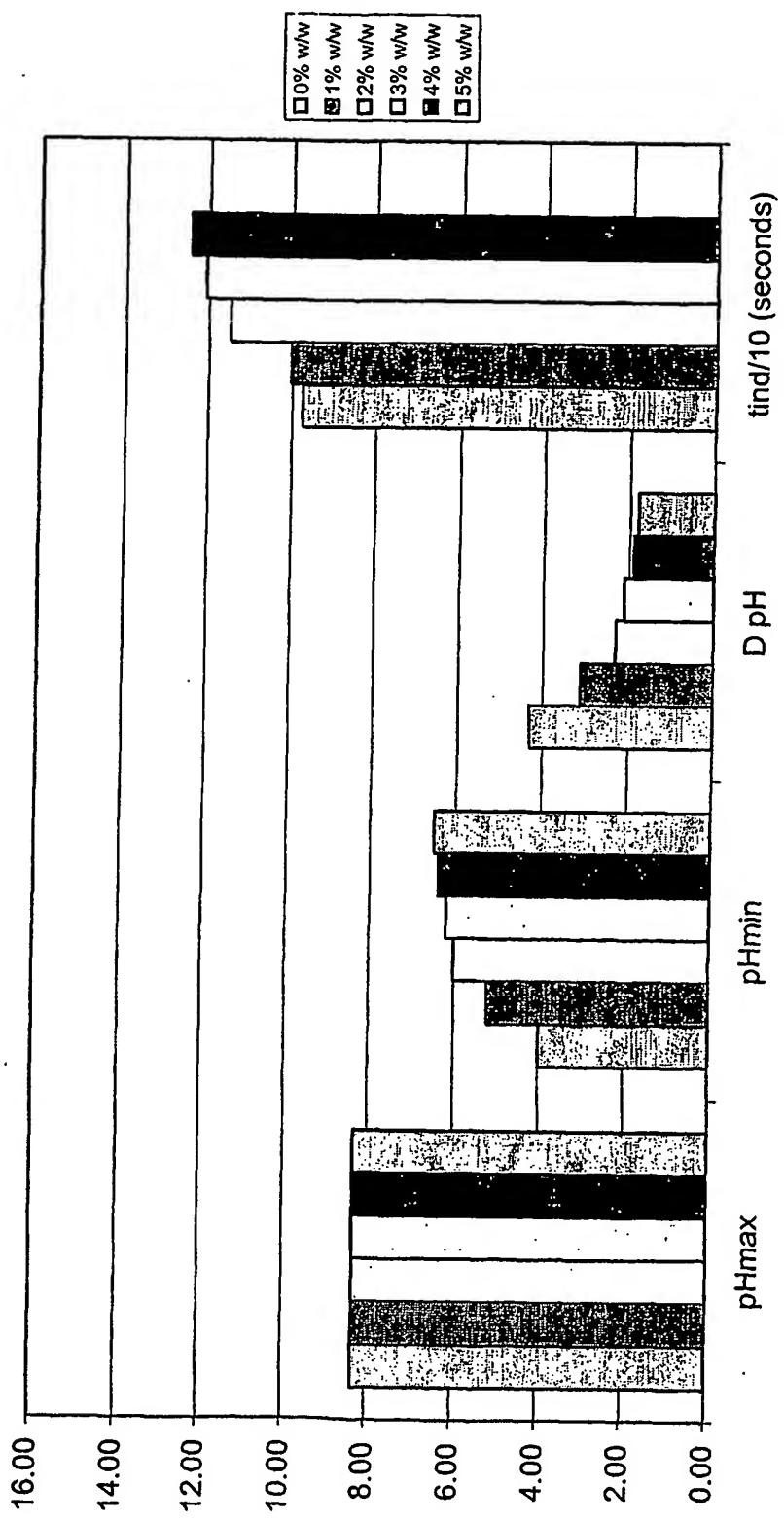


Figure 2

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Compatibility of the hydrogen peroxide-sulfite-bisulfite reaction with sodium lauryl sulfate

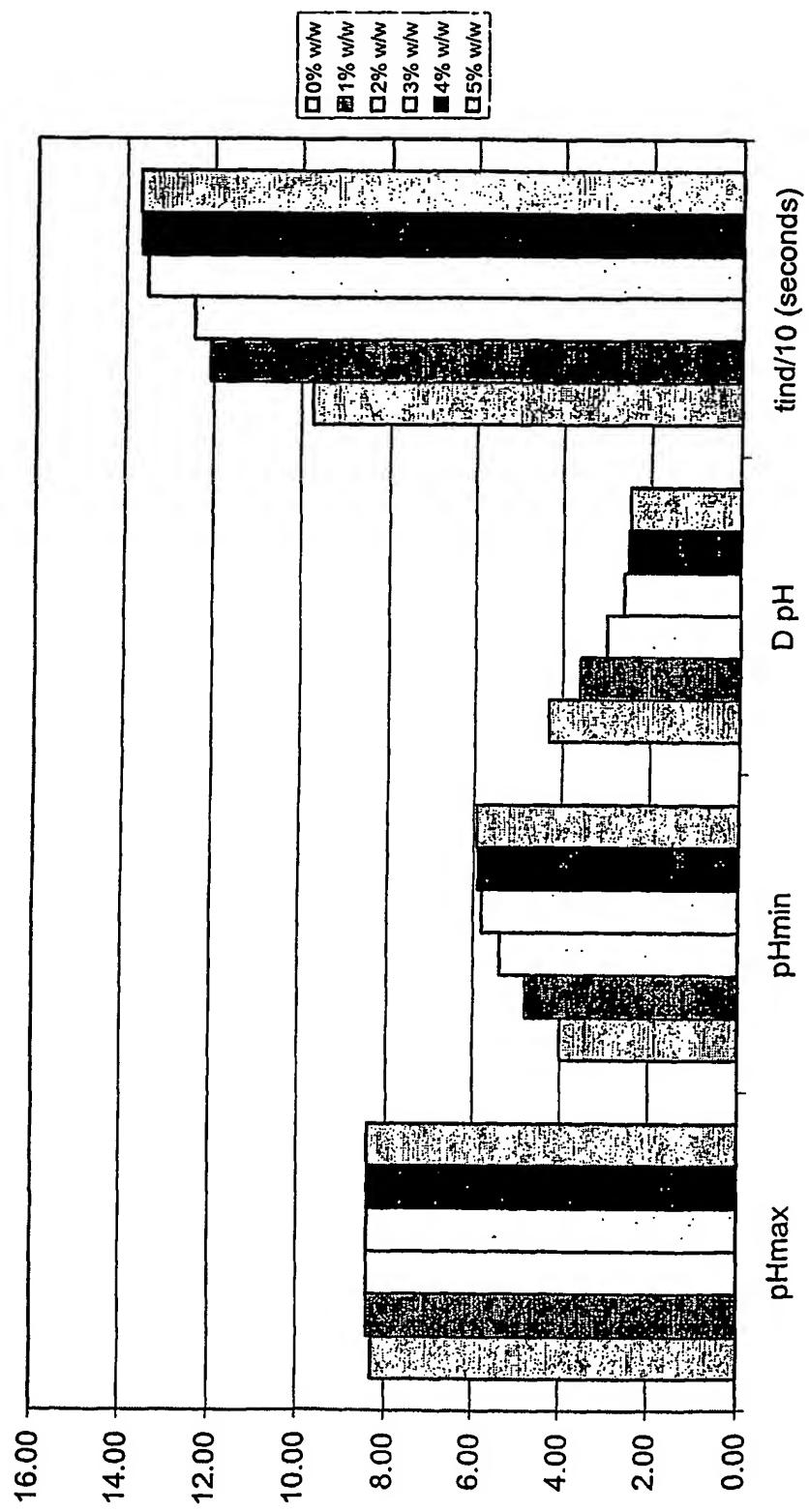


Figure 3

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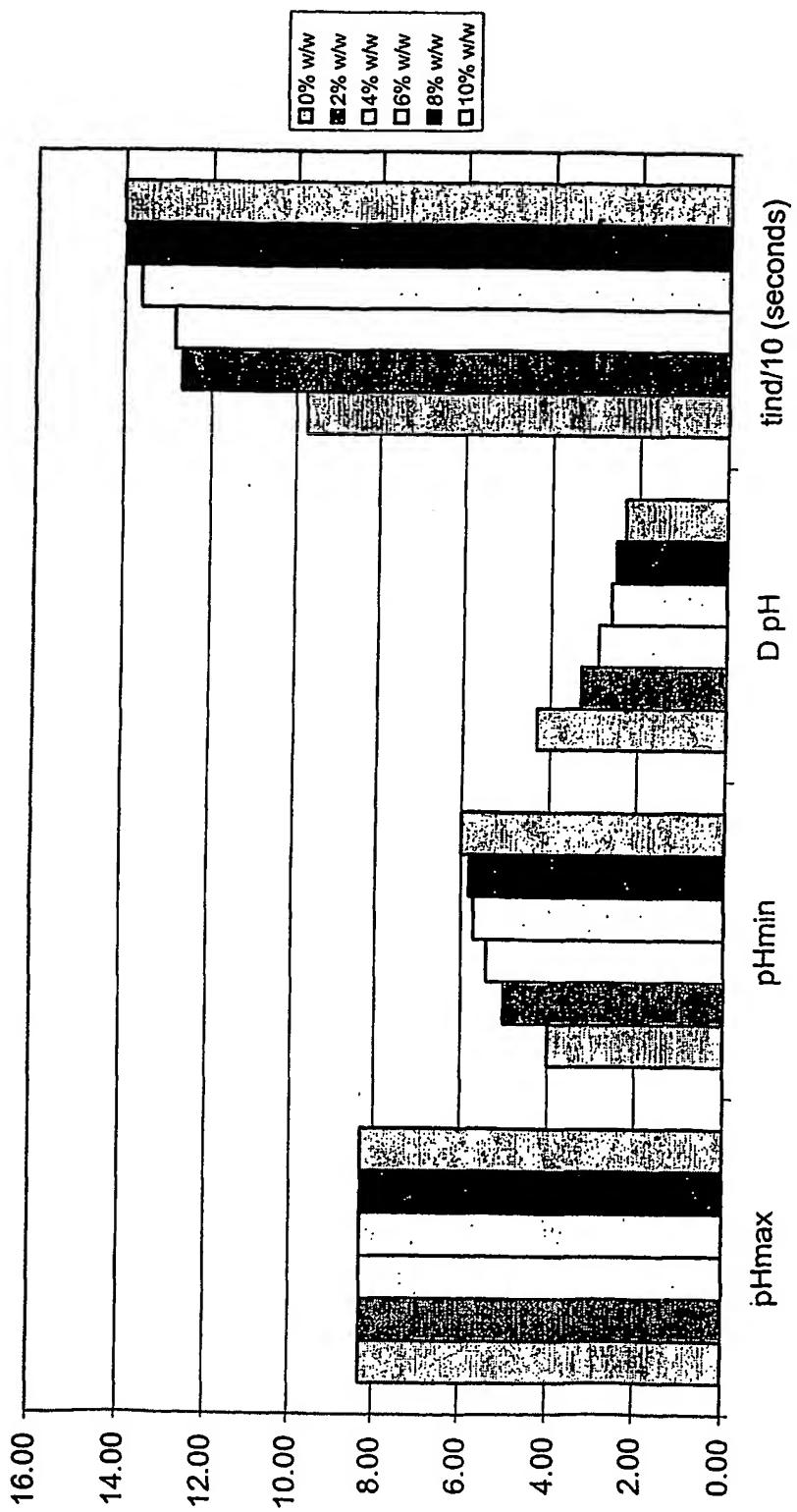
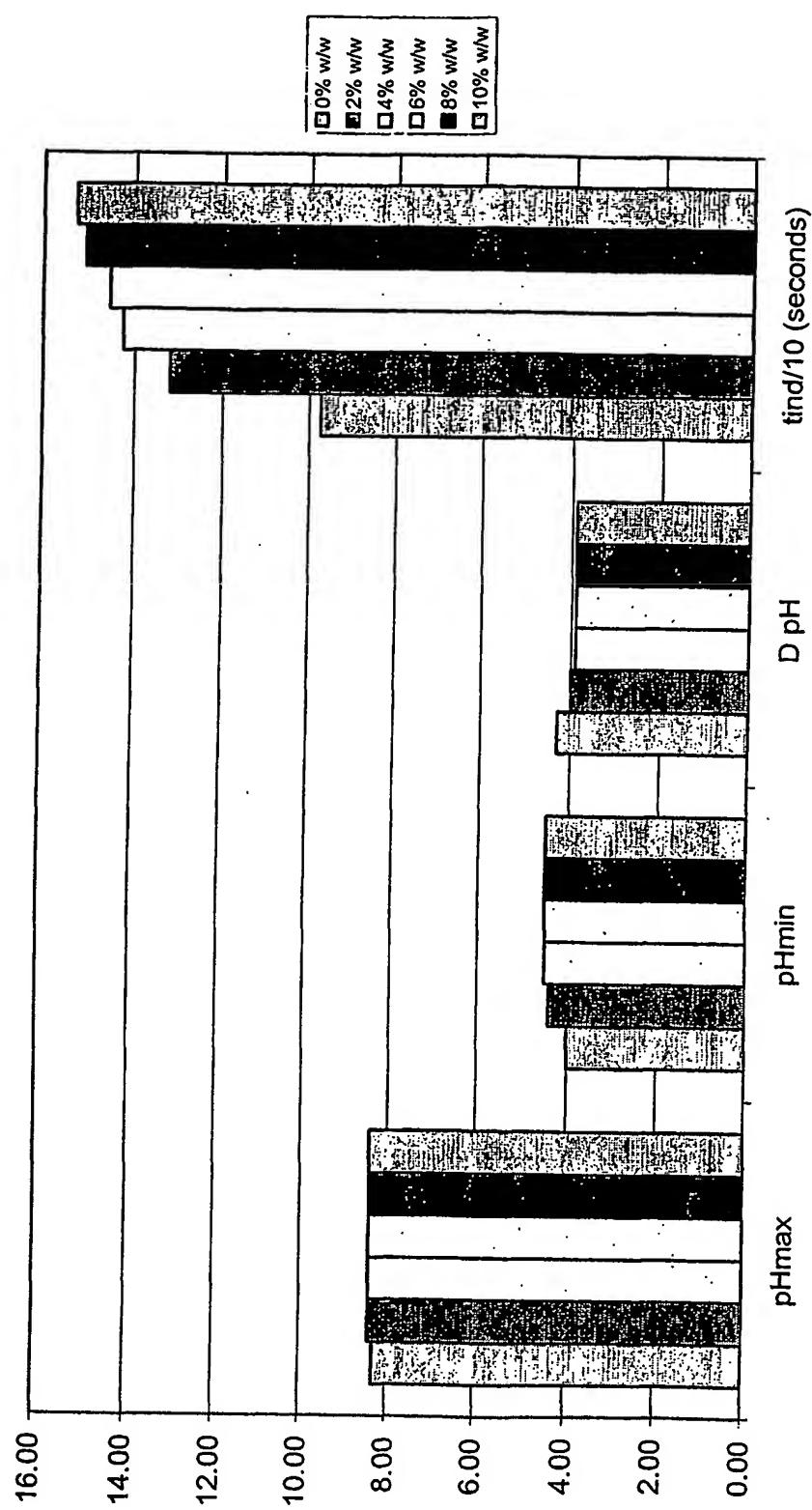


Figure 4

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A. CLASSIFICATION OF SUBJECT MATTER		
IPC 7	C11D3/39	C11D17/00
		C11D17/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	GB 2 000 177 A (AKZO NV) 4 January 1979 (1979-01-04) page 1, line 52 -page 2, line 2 page 2, line 60 -page 3, line 8 page 3, line 33 -page 4, line 3 --- -/-	1-5, 10, 11, 13-15, 20

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- *&* document member of the same patent family

Date of the actual completion of the International search

5 November 2001

Date of mailing of the International search report

15/11/2001

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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